Ultraviolet Absorption and Resonance Raman Spectra of Copper(I) Complexes

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Received January 16, 1986

The importance of Cu(I) centers at the active site of a number of proteins is well documented.[2] However, the fact that the d^{10} metal ion is "invisible" to many of the standard spectroscopic methods used to study metalloproteins hinders investigations of those active sites. Recently, we and others have shown that Cu(I) complexes with heteroaromatic nitrogen ligands exhibit low-lying metal-to-ligand charge-transfer (MLCT) transitions.[3-5] We are therefore examining the spectroscopic properties of Cu(I) complexes in various coordination environments to determine if the MLCT transitions can aid our understanding of the structure of the metal ion site in Cu(I) proteins. We report herein the electronic spectral properties of several two-, three-, and four-coordinate Cu(I) complexes having nitrogen ligands and demonstrate that UV resonance Raman spectroscopy can provide structural information about the complex.

Spectra for a series of copper(I) pyrazole complexes are shown in Figure 1, and complete data for several pyrazole and imidazole[5] complexes and their ligands are summarized in Table I.[6] Intense absorptions in the UV region characterize the spectra for all of these compounds, the highest energy bands being associated with the ligand $\pi \rightarrow \pi^*$ transition. The lower energy bands are Cu(I) → pyrazole (or Cu → imidazole) charge-transfer transitions (vide infra).

The spectra in Figure 1 were obtained on complexes that constitute the series having $(N)_2$, $(N)_3$, and $(N)_4$ donor sets in which at least two of the donors are trisubstituted pyrazoles. The results suggest that changes in the coordination environment have pronounced effects on the energy of the MLCT transitions. In the two-coordinate complexes, a broad shoulder is seen at approximately 240 nm which corresponds to the $d\pi \rightarrow \pi^*$ and $d\sigma^* \rightarrow \pi^*$ transitions. The three-coordinate Cu(I) pyrazole complex exhibits a well-defined band at 254 nm which is assigned as the $d\pi \rightarrow \pi^*$ transition. For this compound the $d\sigma^* \rightarrow \pi^*$ is seen at lower energy, appearing at 302 nm. A single broad band seen for the four-coordinate complexes comprises both the $d\pi \rightarrow \pi^*$ and the $d\sigma^* \rightarrow \pi^*$ transitions.

To corroborate our assignments of the MLCT character of these transitions we have made the Ag(I) analogue for each type of compound. In all cases the MLCT transitions shift to higher energy as expected for the less readily oxidizable silver(I) ion. In addition, we have shown that similar transitions are observed for the two- and three-coordinate imidazole complexes $Cu(4\text{-MeIm})_2^+$[7] and $[Cu(timm)]_2^{2+}$.[5] This latter correlation is necessary to show that the more readily accessible pyrazole complexes can be used in a semiquantitative manner to spectroscopically model the imidazole-ligated site found in proteins.

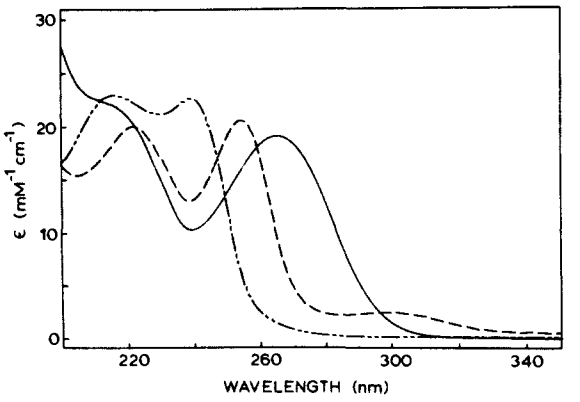

Figure 1. Electronic absorption spectra for $Cu(Me_6trpyn)^+$ (—), $Cu(pza)^+$ (--), and $Cu(TMP)_2^+$ (-·--) in methanol solution.

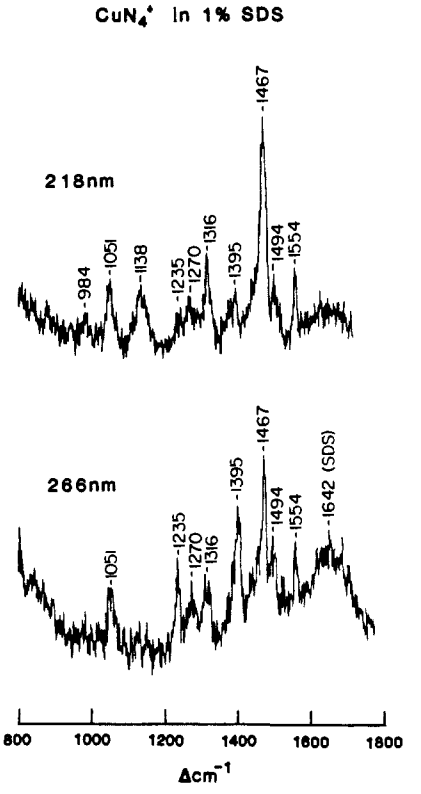

Figure 2. Raman spectrum of $Cu(Me_6trpyn)^+$, 1 mM in a 1% aqueous sodium dodecylsulfate (SDS) suspension, excited at 266 and 218 nm with a H_2-Raman-shifted Nd:YAG laser (see ref 10 for details of the apparatus), showing several resonance-enhanced ring modes of the substituted pyrazole ligand. The SDS suspension (prepared by sonication for 10 min followed by heating in a 75 °C water bath—its absorption spectrum showed the complex to be intact) was used to avoid strong Raman peaks from alcoholic solvents. The 266-nm-excited spectrum shows a broad band at 1642 cm^{-1} due to the SDS micelles.

Figure 2 shows Raman spectra for the four-coordinate complex $Cu(Me_6trpyn)^+$[9] with 266- and 218-nm excitation from a frequency-quadrupled and H_2 Raman-shifted pulsed Nd:YAG laser, using instrumentation described in ref 10. These two wavelengths fall within the charge transfer and intraligand absorption bands, respectively. In both cases resonance enhancement is seen for the ring modes of the substituted pyrazole ligand in the 1000–1600-cm^{-1} region. Both electronic transitions populate the lowest unoccupied pyrazole π^* orbital, leading to distortions of the π-bonds and shifts of the excited-state potential along the ring mode normal coordinates. Differences between the charge transfer and

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(6) Abbreviations used in this paper: pza, bis[2-(1-pyrazolyl)ethyl]amine; trypn, tris[-(1-pyrazolyl)ethyl]amine; DMP, 3,5-dimethylpyrazole; TMP, 1,3,5-trimethylpyrazole; timm, tris[2-(1-methylimidazolyl)]methoxymethane; Im, imidazole; Pz, pyrazole.
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0002-7863/86/1508-5636$01.50/0

Table I. Spectral Data for Copper(I) Complexes and Ligands[a]

complex	λ_{max}[b] (ϵ)[c]	ligand	λ_{max}[b] (ϵ)[c]
two-coordinate[d]			
$Cu(DMP)_2^+$	209 (20.8), 234 (24.8)	DMP	214 (6.4)
$Cu(TMP)_2^+$	215 (23.5), 239 (23.1)	TMP	220 (7.8)
$Cu(4\text{-MeIm})_2^+$	207 (28.2)	4-MeIm	201 (9.7)
three-coordinate			
Cu(pza)+[e]	220 (17.2), 231 (sh), 254 (16.5), 299 (1.6)	pza	220 (13.2)
$[Cu(timm)]_2^{2+}$[f]	232 (28.9), 287 (3.75)	timm	225 (23.7)
four-coordinate[g]			
$Cu(trpyn)^+$	215 (17.2), 261 (16.5)	trpyn	216 (19.8)
$Cu(Me_6trpyn)^+$	218 (21.4), 265 (19.1)	Me_6trpyn	220 (25.1)

[a] In methanol. [b] nm. [c] mM^{-1} cm^{-1}, sh = shoulder. [d] Reference 7. [e] Reference 8. [f] Reference 5. [g] Reference 9.

π-π^* excited states can be seen in the altered enhancement patterns, reflecting different Franck-Condon factors. Thus the 218-nm-excited spectrum is dominated by the 1467-cm^{-1} band, while the 266-nm-excited spectrum has a more even intensity distribution. The relative intensities of the 1235- and 1395-cm^{-1} bands are much higher with 266- than 218-nm excitation. Similar spectra are obtained for the Ag(I) complex with 218- but *not with 266-nm* excitation.

Thus, selecting laser lines which correspond to the MLCT absorption bands of the Cu(I) complex provides specific enhancement of the coordinated ligand modes. This effect should prove useful in probing the structure of the coordination group in reduced copper proteins. Moreover, their UVRR spectra and excitation profiles should aid in delineating the MLCT absorption bands, which are likely to be hidden among the aromatic side-chain absorptions.

Acknowledgment is made to the National Science Foundation (CHE-8317080, TNS and CHE-8106084, TGS) and to the National Institutes of Health (GM 13498, TGS) for support of this work.

Molecular Recognition: Ionic and Aromatic Stacking Interactions Bind Complementary Functional Groups in a Molecular Cleft

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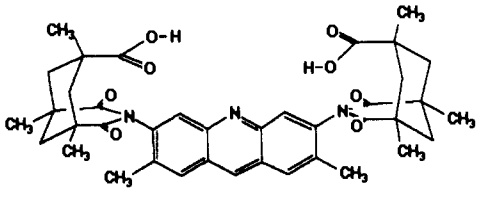
Received May 19, 1986

We recently introduced the model receptor **1** and showed its affinity for molecules of complementary size and shape.[1] The



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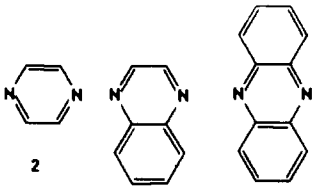
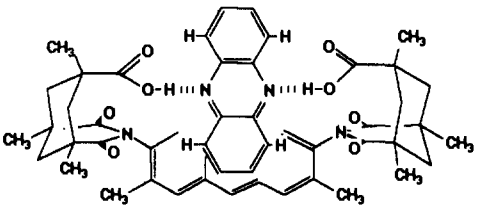


2 **3** **4**

structure features a rapidly assembled *molecular cleft* defined by the convergence of two carboxyl groups and the acridine nitrogen. The cleft provides a highly polar microenvironment in an otherwise lipophilic skeleton, a feature that proves useful in the transport of amino acids across liquid membranes.[2] In this paper we explore the selectivity that the system shows toward molecules of complementary functionality.

Table I Association Constants[a] for Complexes of **1** ($CDCl_3$, 25 °C)



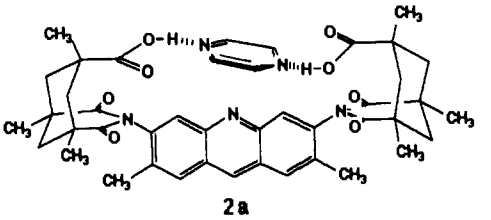
4a

5

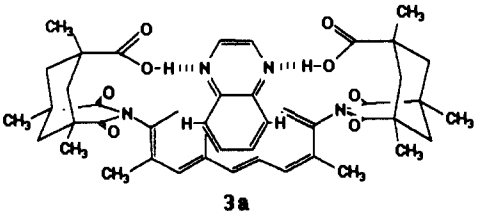
base	K_a, M^{-1} L	pK_a[b](BH+)
pyrazine (**2**)	1.4×10^3	0.65
quinoxaline (**3**)	23×10^3	0.56
phenazine (**4**)	2.2×10^3	1.2
pyrimidine (**5**)	0.7×10^3	1.3
quinazoline (**6**)	1.6×10^3	1.9[c]
imidazoline (**7**)	$K_1 = 1.0 \times 10^6$, K_2[d] $= 5.5 \times 10^4$	6.9
benzmidazole (**8**)	$K_1 = 1.5 \times 10^4$, K_2[d] $= 7.5 \times 10^3$	5.5
purine[e] (**9**)	$\sim 8 \times 10^3$	2.4
pyridine	$K_1 = 1.2 \times 10^2$, K_2[d] = <1	5.2

[a] Obtained from Eadie-Hofstee plots[4] involving chemical shift changes as a function of receptor/substrate ratios. Saturation of the receptor (>95% sites occupied) was attained with all bases except pyridine. [b] Albert, A. In *Physical Methods in Heterocyclic Chemistry*; Katritsky, A., Ed.; Academic Press: New York, 1963; Vol. I, chapter 1. [c] For the unhydrated form: *The Chemistry of Heterocyclic Compounds*; Brown, D. J., Ed.; Interscience: New York, 1967; Vol. 24. Part 2 (Quinalzolines), Ch. II. [d] M^{-2} L^2. [e] Low solubility of this base required sufficiently high dilution that NMR shifts were difficult to assess.

The binding of **1** to heterocyclic diamines was studied by using the NMR techniques described previously,[1] and association constants are reported in Table I. For example, the binding of aromatic amines such as pyrazine **2** causes upfield shifts for the signals for the interior protons of the cleft (H_4, H_5) whereas mere deprotonation by conventional bases such as triethylamine causes downfield shifts in these signals. The most likely structure for the pyrazine complex involves a perpendicular arrangement of the two aromatic systems shown in **2a**. The selectivity for the



2a



3a

diamine pyrazine vs. pyridine can be seen in Table I: **1** recognizes and preferentially complexes pyrazine *in the presence of* the stronger base, pyridine.

Similiar studies involving the benzo derivatives of pyrazine reveal how stacking interactions and steric effects alter association constants. Thus, quinoxaline **3** shows a 15-fold enhancement in binding over **2**, and the stacking interaction between aromatic

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